

A generalized molecular theory for nematic liquid crystals formed by non-cylindrically symmetric molecules

O. Kayacan*

*Physics Department, Art and Science Faculty, Celal Bayar University,
Muradiye/Manisa-TURKEY*

Abstract

Many molecular theories of nematic liquid crystals consider the constituent molecules as cylindrically symmetric. In many cases, this approximation may be useful. However the molecules of real nematics have lower symmetry. Therefore a theory was developed (Mol. Phys. 30 (1975) 1345) for an ensemble of such particles based upon a general expansion of the pairwise intermolecular potential together with the molecular field approximation. In this study, we would like to handle this molecular field theory by using Tsallis thermostatics which has been commonly used for a decade to study the physical systems. With this aim, we would like to investigate the dependence of the order parameters on temperature and would like to report the variation of the critical values of the order parameters at the transition temperature with the entropic index.

PACS Number(s): 05.20.-y, 05.70.-a, 61.30.Cz, 61.30. Gd.

Keywords: Tsallis thermostatics, Maier-Saupe theory, nematic liquid crystals, non-cylindrically symmetrical molecules.

*e-mail: ozhan.kayacan@bayar.edu.tr

I. INTRODUCTION

It is well known that an essential characteristic of compounds forming liquid crystals is the rod-like shape of their constituent molecules, with an high length to breadth ratio. Therefore the molecules are supposed to be cylindrically symmetrical. For example, the ordering matrix which is often used to describe the partial alignment in a mesophase, contains only one independent element and this can be determined by some techniques [1]. The fact that the molecular cylindrical symmetry is assumed is appealing to a statistical mechanician, because the pairwise anisotropic intermolecular potential required in any calculation is simple for such particles [2]. However the molecules, in fact, are lath-like and thus do not possess the high symmetry.

The ordering matrix has two principal components and therefore these components are required to describe the orientational order of a uniaxial mesophase composed of lath-like molecules. In this sense, the deviation of this ordering matrix from cylindrical symmetry was found to be significant [3]. The importance of deviations from cylindrical symmetry may be inferred from unambiguous determinations of the ordering matrix for rod-like molecules, such as 4,4' – *dichlorobiphenyl* [4]. Moreover it is found that these matrices are comparable to those estimated for a pure mesophase [3].

There are some studies in which the consequences of deviations from molecular cylindrical symmetry are investigated. It is shown that a system consisting of particles with a lower symmetry than $D_{\infty h}$ is capable of existing either as a uniaxial or a biaxial liquid crystal [5]. The possible existence of a biaxial phase is studied in detail for a system of hard rectangular plates using a lattice model [6], the Landau approach [7] and the molecular field approximation [8]. The deviations of the ordering matrix from cylindrical symmetry is clearly determined by the molecular symmetry and the element of the ordering matrix for the long axis will also be influenced by the form of the pseudo-intermolecular potential. The calculations of the ordering matrix for an ensemble of hard rectangular particles is performed in [9]. It must be emphasized that although these calculations are of some interest, they may

not be particularly realistic because some experiments indicate that dispersion forces may make a dominant contribution to the anisotropic intermolecular potential [9]. Considering the cases above, Luckhurst et al. developed a theory [10] for non-cylindrically symmetric molecules interacting via a completely general intermolecular potential within molecular field approximation.

For a decade, nonextensive statistics has an increasing interest and recently Tsallis thermostatics (TT) has been applied to the nematic-isotropic transition [11-13] as a nonextensive statistics. In [11], the Maier-Saupe mean field theory has been generalized within TT and applied to a nematic liquid crystal, para-azoxyanisole. In the other study, [12], the effects of the nonextensivity on the dimerization process has been studied, and finally the mean field theory of anisotropic potential of rank $L = 4$ has been generalized within TT and the effect of the nonextensivity on the order parameters has been illustrated in [13]. Up to now, the mean field theories for uniaxial nematogens formed by cylindrically symmetric molecules have been studied by using TT. In this manner, we aim, in this study, to enlarge the applications of TT to the liquid crystal systems and to handle Luckhurst et al.'s theory which considers the molecules to be non-cylindrically symmetric. In doing so, we first give some essential properties of Luckhurst et al.'s theory. Then we mention on TT and its axioms. Finally, we apply TT to the Luckhurst et al.'s theory and some possible concluding remarks are made. We must emphasize that we would like to give only the possible contributions of the nonextensivity to the theory. So we must keep in mind that since one relies on the generalized theory or not, more extensional studies related with it must be performed in the nematic-isotropic transition. However, we believe that this study is sufficient to give motivation for further applications of TT to the liquid crystals.

A. The Molecular Theory for Uniaxial Nematics Formed by Non-cylindrically Symmetric Molecules

The intermolecular potential for particles of general shape is given by [10]

$$U_{12} = \sum u_{L_1 L_2 m_1 m_2 n_1 n_2}(r_{12}) D_{m_1, n_1}^{(L_1)}(\Omega_{1-R}) D_{m_2, n_2}^{(L_2)}(\Omega_{2-R}) \quad (1)$$

in a product basis of Wigner rotation matrix [14], where r_{12} is the distance between molecules 1 and 2. The orientation of molecule Ω_{1-R} in a coordinate system containing the intermolecular vector as the z axis is denoted by Ω_{i-R} . This potential energy is invariant under rotation of the coordinate system about z axis. Therefore the summation in Eq.(1) can be restricted as follows [10]:

$$U_{12} = \sum u_{L_1 L_2 m n_1 n_2}(r_{12}) D_{m, n_1}^{(L_1)}(\Omega_{1-R}) D_{-m, n_2}^{(L_2)}(\Omega_{2-R}). \quad (2)$$

In what follows, the redundant subscripts on the coefficient $u(r_{12})$ will be suppressed. Because it is convenient to define the molecular orientation in terms of a common coordinate system, the potential energy U_{12} could be transformed to a laboratory frame. The choice of this coordinate system is determined according to the symmetry of the liquid crystal phase, so for a uniaxial mesophase, the laboratory z axis can be taken to be parallel to the symmetry axis of the mesophase. The transformation of U_{12} is carried out by performing the rotation from the intermolecular vector to the molecule in two steps using the relationship

$$D_{m, n}^{(L)}(\Omega_{1-R}) = \sum_j D_{j, m}^{(L)*}(\Omega_{R-L}) D_{j, n}^{(L)}(\Omega_{1-R}), \quad (3)$$

where the subscript $R - L$ is the rotation from the laboratory to the intermolecular frame, $1 - L$ denotes that from the laboratory to the molecule coordinate system. Then the intermolecular potential can be written as

$$U_{12} = \sum u_{L_1 L_2 m n_1 n_2}(r_{12}) D_{j_1, n_1}^{(L_1)}(\Omega_{1-L}) D_{j_2, n_2}^{(L_2)}(\Omega_{2-L}) D_{j_1, m}^{(L_1)*}(\Omega_{R-L}) D_{j_2, -m}^{(L_2)*}(\Omega_{R-L}). \quad (4)$$

If the distribution function for the intermolecular vector is independent of orientation, then one could use the orthogonality of the rotation matrices to evaluate the ensemble average:

$$\overline{D_{j_1, m}^{(L_1)*}(\Omega_{R-L}) D_{j_2, -m}^{(L_2)*}(\Omega_{R-L})} = \frac{(-1)^{j_2+m} \delta_{j_1, -j_2} \delta_{L_1, L_2}}{2L_1 + 1}. \quad (5)$$

The partially averaged potential may then be written as

$$U_{12} = \sum \frac{(-1)^{j+m}}{2L+1} u_{Lmn_1n_2}(r_{12}) D_{j,n_1}^{(L)}(\Omega_{1-L}) D_{-j,n_2}^{(L)}(\Omega_{2-L}). \quad (6)$$

Then now it is the time to average over the orientations adopted by particle 2. However one needs $\overline{D_{-j,n_2}^{(L)}}$. This average is taken to be independent of the orientation of molecule 1 within the molecular field approximation and it is to be identified with the normal ensemble average. Since we only consider a uniaxial mesophase, $\overline{D_{-j,n_2}^{(L)}}$ vanishes when $j \neq 0$ and L is even. In this manner, the potential is reduced to the following form:

$$U_{12} = \sum_{L, \text{even}} \frac{(-1)^m}{2L+1} u_{Lmn_1n_2}(r_{12}) D_{0,n_1}^{(L)}(\Omega_{1-L}) \overline{D_{0,n_2}^{(L)}(\Omega_{2-L})}, \quad (7)$$

where the summation is over $L \geq 0$ (L even). The scalar contribution could be ignored because we would only like to study the orientational properties of the mesophase. The average of the orientational pseudo-potential for molecule 1 is given by

$$U_1 = \sum_{L, \text{even}} \frac{(-1)^m}{2L+1} \overline{u}_{Lmn_1n_2} D_{0,n_1}^{(L)}(\Omega_{1-L}) \overline{D_{0,n_2}^{(L)}}. \quad (8)$$

The expansion coefficients in Eq.(8) are defined by

$$\overline{u}_{Lmn_1n_2} = \frac{\int u_{Lmn_1n_2}(r_{12}) \exp(-U_o(\mathbf{r}_1 \dots \mathbf{r}_N)/kT) \mathbf{dr}_1 \dots \mathbf{dr}_N}{\int \exp(-U_o(\mathbf{r}_1 \dots \mathbf{r}_N)/kT) \mathbf{dr}_1 \dots \mathbf{dr}_N}, \quad (9)$$

where $U_o(\mathbf{r}_1 \dots \mathbf{r}_N)$ is the scalar potential of the ensemble [10,15].

The pseudo-potential is conveniently written as

$$U(\beta\gamma) = \sum_{L, \text{even}} c_{Ljp} \overline{D_{0,p}^{(L)}} D_{0,j}^{(L)}(\beta\gamma), \quad (10)$$

where

$$c_{Ljp} = \sum_m (-1)^m \frac{\overline{u}_{Lmjp}}{2L+1}, \quad (11)$$

with β and γ is the Euler angles and define the orientation of the director in the molecular coordinate system.

Luckhurst et al. made some comments in [10] on this form of the pseudo-potential and the symmetry properties of the coefficients c_{Ljp} . Because Luckhurst et al. investigated the

influence of deviations from molecular cylindrical symmetry on various orientational order parameters for a uniaxial nematic mesophase, they tried to minimize the number of the variables in the calculation without any loss of the essential physics. As a first approximation, they considered only those terms with L equal to 2 in the expansion of the pseudo-potential. The neglect of terms higher than quadratic could be a good approximation, since similar assumptions for cylindrically symmetric molecules had led to results in reasonable accord with experiment [10,16]. As mentioned in [10], the number of expansion coefficients are reduced by appealing to some specific model for the interactions or by imposing symmetry restrictions on the molecules. If one follows Straley [9] and takes the molecules to be hard rectangular parallelepipeds, then the coefficients c_{2jp} are independent of the sign of either p or j and zero if either of these subscripts is odd, that is

$$c_{200} = [-2B(W^2 + L^2) - 2W(L^2 + B^2) + L(W^2 + B^2) + 8WBL] / 3, \quad (12)$$

$$c_{220} = (L^2 - BW)(B - W) / \sqrt{6}, \quad (13)$$

$$c_{222} = -L(W - B)^2 / 2, \quad (14)$$

where L is the length, B the breadth and W the width of the molecule. It must be noted that this parametrization is only approximate [9] and also anisotropic repulsive forces are probably not dominant in determining the behaviour of real nematics. Therefore assuming the molecules to interact via dispersion forces, the expressions for c_{2jp} could be derived.

The similar restriction can be imposed on the expansion coefficients c_{2jp} , without appealing to specific forms of the intermolecular interactions, by using more formal arguments based on the molecular symmetry and its influence on the pair potential. For example, if each molecule has a centre of symmetry, then [10]

$$\begin{aligned} u_{L_1 L_2 m n_1 n_2}(r_{12}) &= (-1)^{L_1 - n_1} u_{L_1 L_2 m - n_1 n_2}(r_{12}) = (-1)^{L_2 - n_2} u_{L_1 L_2 m n_1 - n_2}(r_{12}) \\ &= (-1)^{L_1 + L_2 - n_1 - n_2} u_{L_1 L_2 m - n_1 - n_2}(r_{12}) \end{aligned} \quad (15)$$

and consequently

$$c_{Ljp} = (-1)^j c_{L-jp} = (-1)^p c_{Lj-p} = (-1)^{j+p} c_{L-j-p}. \quad (16)$$

In addition, if the molecules also possess a plane of symmetry orthogonal to their z axes, then

$$\begin{aligned} u_{L_1 L_2 m n_1 n_2}(r_{12}) &= (-1)^{L_1} u_{L_1 L_2 m - n_1 n_2}(r_{12}) = (-1)^{L_2} u_{L_1 L_2 m n_1 - n_2}(r_{12}) \\ &= (-1)^{L_1 + L_2} u_{L_1 L_2 m - n_1 - n_2}(r_{12}) \end{aligned} \quad (17)$$

and

$$c_{Ljp} = (-1)^L c_{L-jp} = (-1)^L c_{Lj-p} = c_{L-j-p}. \quad (18)$$

However Eqs.(16,18) can only be consistent when both p and j have even values. Moreover the coefficients are independent of the sign of p and j .

Then the pseudo-potential may be written as

$$U(\beta\gamma) = \sum_{L, |p|, |j| \text{ (even)}} c_{Ljp} \left[D_{0,p}^{(L)} + D_{0,-p}^{(L)} \right] \left[D_{0,j}^{(L)}(\beta\gamma) + D_{0,-j}^{(L)}(\beta\gamma) \right] / (1 + \delta_{0j})(1 + \delta_{0p}). \quad (19)$$

according to the restrictions above. If limiting the summation to those terms with L equal to 2, one has

$$\begin{aligned} U(\beta\gamma) &= \left[c_{200} \overline{d_{0,0}^{(2)}} + 2c_{220} \overline{d_{0,2}^{(2)} \cos(2\gamma)} \right] d_{0,0}^{(2)}(\beta) \\ &\quad + 2 \left[c_{200} \overline{d_{0,0}^{(2)}} + 2c_{222} \overline{d_{0,2}^{(2)} \cos(2\gamma)} \right] d_{0,2}^{(2)}(\beta) \cos(2\gamma), \end{aligned} \quad (20)$$

where $d_{m,n}^{(2)}(\beta)$ is a reduced Wigner rotation matrix [14]. The second rank order parameters $\overline{d_{0,0}^{(2)}}$ and $\overline{d_{0,2}^{(2)} \cos(2\gamma)}$ in this expression are related to the principal elements of the ordering matrix by

$$S_{zz} = \overline{d_{0,0}^{(2)}} \quad (21)$$

and

$$S_{xx} - S_{yy} = \sqrt{6} \overline{d_{0,2}^{(2)} \cos(2\gamma)}. \quad (22)$$

The order parameter $\overline{d_{0,2}^{(2)} \cos(2\gamma)}$ indicates the deviation of the ordering matrix from cylindrical symmetry. For simplicity, it is convenient to write the pseudo-potential as

$$U(\beta\gamma) = -kT \left[a d_{0,0}^{(2)}(\beta) + b d_{0,2}^{(2)}(\beta) \cos(2\gamma) \right], \quad (23)$$

where

$$a = - \left[c_{200} \overline{d_{0,0}^{(2)}} + 2 c_{220} \overline{d_{0,2}^{(2)} \cos(2\gamma)} \right] / kT \quad (24)$$

and

$$b = - \left[2 c_{220} \overline{d_{0,0}^{(2)}} + 4 c_{222} \overline{d_{0,2}^{(2)} \cos(2\gamma)} \right] / kT. \quad (25)$$

The partition function for this single particle potential is then given by

$$Z = \int_0^{2\pi} \int_0^\pi \exp \left[a d_{0,0}^{(2)}(\beta) + b d_{0,2}^{(2)}(\beta) \cos(2\gamma) \right] \sin \beta d\beta d\gamma. \quad (26)$$

The orientational molar potential energy and the molar entropy are given as follows

$$U = -(RT/2) \left[a \overline{d_{0,0}^{(2)}} + b \overline{d_{0,2}^{(2)} \cos(2\gamma)} \right], \quad (27)$$

$$S = -R \left[a \overline{d_{0,0}^{(2)}} + b \overline{d_{0,2}^{(2)} \cos(2\gamma)} \right] + R \ln(Z). \quad (28)$$

respectively. Then the orientational molar free energy is straightforward:

$$F_m = \frac{RT}{2} \left[a \overline{d_{0,0}^{(2)}} + b \overline{d_{0,2}^{(2)} \cos(2\gamma)} \right] - RT \ln(Z). \quad (29)$$

The order parameters are calculated from the equations below:

$$\overline{d_{0,0}^{(2)}} = \frac{\int_0^{2\pi} \int_0^\pi d_{0,0}^{(2)}(\beta) \exp \left[a d_{0,0}^{(2)}(\beta) + b d_{0,2}^{(2)}(\beta) \cos(2\gamma) \right] \sin \beta d\beta d\gamma}{Z} \quad (30)$$

and

$$\overline{d_{0,2}^{(2)} \cos(2\gamma)} = \frac{\int_0^{2\pi} \int_0^\pi d_{0,2}^{(2)}(\beta) \cos(2\gamma) \exp \left[a d_{0,0}^{(2)}(\beta) + b d_{0,2}^{(2)}(\beta) \cos(2\gamma) \right] \sin \beta d\beta d\gamma}{Z}. \quad (31)$$

It is worthwhile to note that $\overline{d_{0,0}^{(2)}}$ in Eq.(30) is simply $\overline{P_2}$, (P_2 is the second Legendre polynomial). The free energy F_m will be a minimum provided the consistency equations for these order parameters are satisfied. With the aid of Eqs.(24,25), one can write the following equations:

$$a = -\alpha \left[d_{0,0}^{(2)} + 2\lambda d_{0,2}^{(2)} \cos(2\gamma) \right], \quad (32)$$

and

$$b = 2\lambda a, \quad (33)$$

where

$$\alpha = -c_{200}/kT. \quad (34)$$

λ in Eq.(34) is the ratio c_{220}/c_{200} and it is a measure of the deviation from cylindrical symmetry. If λ is taken to be zero, the theory reduced to the Maier-Saupe mean field theory.

Now we would like to give the description of Tsallis thermostatics with its axioms below.

B. Generalization of the theory

Tsallis thermostatics (TT) has been extensively used to investigate the concepts of statistical mechanics and thermodynamics. In this context, it has been applied to various phenomena [17] and TT seems to be appropriate for the study of nonextensive systems. As mentioned above, we have chosen the nematic-isotropic transition as an application area of TT in earlier studies [11-13] and the present study would be the extensional study to investigate the nematic liquid crystals. In all of these earlier studies, we consider that the uniaxial nematic liquid crystals are formed by cylindrically symmetric molecules. However, we wonder in this study that if the mesophase could be formed by non-cylindrically symmetric molecules, how does the nonextensivity affect the nematic-isotropic transition? Therefore our starting point is Luckhurst et al.'s theory [10] which is a molecular field theory and assumes the molecules of the nematic liquid crystals to be non-cylindrical and we examine the effects of the nonextensivity on the nematic-isotropic transition by considering this molecular field theory.

The understanding of the basic principles and properties of TT has gain fundamental importance. In this manner, Tsallis et al. have studied the role of the constraint within TT. Tsallis proposed an entropy definition in 1988 [18]:

$$S_q = k \frac{1 - \sum_{i=1}^W p_i^q}{q - 1} \quad (q \in \mathfrak{R}), \quad (35)$$

where k is a constant, p_i is the probability of the system in the i microstate, W is the total number of configurations and q is called the entropic index whose meaning will be given below. In the limit $q \rightarrow 1$, the entropy defined in Eq.(35) reduced to the Boltzmann-Gibbs (BG) entropy. In other words, TT contains Boltzmann-Gibbs statistics as a special case with $q = 1$. As well known, BG statistics is a powerful one to study a variety of the physical systems. However, it fails for the systems which (i) have long range interactions, (ii) have long range memory effects and (iii) evolve in multi-fractal space-time. The systems which has these properties is called "nonextensive" and if a system does obey these restrictions, BG statistics seems to be inappropriate and one might need a nonextensive formalism to study on the physical system.

It will be useful to write the pseudo-additivity entropy rule,

$$S_q(A + B)/k = (S_q(A)/k) + (S_q(B)/k) + (1 - q) (S_q(A)/k) (S_q(B)/k), \quad (36)$$

which reflects the character of the entropic index q and also of the nonextensivity. In this equation, A and B are two independent systems. Since all cases $S_q \geq 0$ (which is called nonnegativity property), $q < 1$, $q = 1$ and $q > 1$, correspond to superadditivity, additivity and subadditivity respectively.

Because of some unfamiliar consequences of first two energy constraints discussed in [13,19], Tsallis et al. present the third internal energy constraint as follows:

$$\frac{\sum_{i=1}^W p_i^q \varepsilon_i}{\sum_{i=1}^W p_i^q} = U_q^{(3)}. \quad (37)$$

This choice is commonly considered to study physical systems and is denoted as the Tsallis-Mendes-Plastino (TMP) choice. The optimization of Tsallis entropy given by Eq.(35) according to the third choice of the energy constraint results in

$$p_i^{(3)} = \frac{\left[1 - (1 - q)\beta(\varepsilon_i - U_q^{(3)}) / \sum_{j=1}^W (p_j^{(3)})^q\right]^{\frac{1}{1-q}}}{Z_q^{(3)}} \quad (38)$$

with

$$Z_q^{(3)} = \sum_{i=1}^W \left[1 - (1 - q)\beta(\varepsilon_i - U_q^{(3)}) / \sum_{j=1}^W (p_j^{(3)})^q\right]^{\frac{1}{1-q}}. \quad (39)$$

Therefore the q -expectation value of any observable is defined as

$$\langle A_i \rangle_q = \frac{\sum_{i=1}^W p_i^q A_i}{\sum_{i=1}^W p_i^q}, \quad (40)$$

where A represents any observable quantity which commutes with Hamiltonian. As can be expected, when $q = 1$, the q -expectation value of the observable reduces to the conventional one. At this stage, the important point is to solve Eq.(40) which is an implicit one, and Tsallis et al. suggest two different approaches; "*iterative procedure*" and " $\beta \rightarrow \beta$ " transformation. The nonextensivity, in fact, appears in systems where long range interactions and/or fractality exist, and such properties have been invoked in recent models of manganites [20,21] as well as in the interpretation of experimental results. These properties are also appear in [22] where the role of the competition between different phases to the physical properties of these materials is emphasized. The formation of micro-clusters of competing phases, with fractal shapes, randomly distributed in the material is considered in [23,24], and the role of long range interactions to phase segregation [25,26].

If we look at the recent studies in which TT is employed, we see also that the entropic index is frequently established from the dynamics of the system under consideration analytically. Some of such studies are: Boghosian et al.'s study [27] for the incompressible Navier-Stokes equation in Boltzmann lattice models, Baldovin et al.'s studies [28,29] at the edge of chaos for the logistic map universality class, Oliveira et al.' studies [20,21] on manganites.

According to these axioms of TT given above, the order parameters are calculated by using Eq.(40) instead of Eqs.(30) and (31). The exponential form of any function, say x , is given by

$$\exp_q(x) = [1 + (1 - q)x]^{\frac{1}{1-q}} \quad (41)$$

in Tsallis thermostatics. Substituting this equation in the calculation, Eq.(40) is employed and then the self-consistent equations are solved to obtain the order parameters.

The generalized free energy then follows within TT:

$$(F_m)_q = \frac{RT}{2} \left[a \left(\overline{d_{0,0}^{(2)}} \right)_q + b \left(\overline{d_{0,2}^{(2)} \cos(2\gamma)} \right)_q \right] - RT \ln_q(Z_q), \quad (42)$$

where $\ln_q(x) = (Z_q^{(1-q)} - 1)/(1 - q)$.

Now it is the time to give the results of application of TT to the Luckhurst et al.'s theory presented above.

II. RESULTS AND DISCUSSION

The first stage in our calculation is the identification of the transition from the uniaxial nematic phase to the isotropic phase. This may be accomplished for a given molecular symmetry by determining the value of α at which the orientational free energy vanishes, provided there is no volume change at the transition. The results of such calculations are listed Tables (1-3). Table 1 shows the transition temperatures, the critical values of order parameters $\overline{d_{0,0}^{(2)}}$ and $\overline{d_{0,2}^{(2)} \cos(2\gamma)}$ at the transition temperature and the entropy changes at the transition concerning $\lambda = 0.1$ for some values of q . We can see immediately that increasing the entropic index increases α_K and so decreases the nematic-isotropic transition temperature for constant c_{200} . Similar behaviour is also seen from Tables (2) and (3) concerning $\lambda = 0.2$ and 0.3 respectively. Also we see from Tables (1-3) that increasing the entropic index increases the order parameter $\overline{d_{0,0}^{(2)}}$ at the transition for $\lambda = 0.1, 0.2$ and 0.3 . However there is a somewhat suprising result that as q is increased, the secondary order parameter $\overline{d_{0,2}^{(2)} \cos(2\gamma)}$ also increases at the transition for $\lambda = 0.2, 0.3$ while this is not the case for $\lambda = 0.1$, that is, the secondary order parameter decreases with increasing q for $\lambda = 1$. We also observe from the Tables (1-3) that the entropy changes at the transition increases with increasing q .

In Fig.(1), we illustrate the dependence of the order parameter $\overline{d_{0,0}^{(2)}}$ and on reduced temperature for some q values, with $\lambda = 0.1$ only. The results are plotted as a function of the reduced variable (α/α_K) which is identical to the reduced temperature T/T_K provided the coefficients c_{2jp} are themselves independent of temperature. We observe that as q increased, the transition becomes more markedly first-order. It is well known from [10] that the effect of introducing deviations from cylindrical symmetry is to lower the curves for $\lambda = 0, 0.1, 0.2$ and 0.3 respectively, as well as changing their slopes. It is clear from Fig.(1) that as q is decreased, the similar behaviour is also seen, that is, the slope of the curve for $\lambda = 0.1$ decreases with increasing the entropic index q . The similar behaviour could also expected for other λ values ($\lambda = 0, 0.1, 0.3$). The secondary order parameter $\overline{d_{0,2}^{(2)} \cos(2\gamma)}$ is plotted as a function of $\overline{d_{0,0}^{(2)}}$, that is $\overline{P_2}$, in Fig.(2) with $\lambda = 0.2$ for various values of the entropic index. These results exhibit an unusual behaviour, for the order parameter $\overline{d_{0,2}^{(2)} \cos(2\gamma)}$ is observed to increase with increasing $\overline{P_2}$ pass through a maximum and then decrease. It is interesting to note that as q is decreased, the maximum value of the secondary order parameter assumes a higher value than those concerning lower value of q .

Another important point is that Maier-Saupe theory gives a universal value of the $\overline{d_{0,0}^{(2)}}$ at the transition temperature $((\overline{P_2})_c = 0.429)$. However both Luckhurst et al.'s theory and the generalized form of the Maier-Saupe theory, including the present study, assume different values of this order parameter with changing λ and q parameters. This fact is consistent with experiment in that experimental values of $\overline{d_{0,0}^{(2)}}$ for various nematics assume in a range of $0.25 - 0.5$ [30]. While λ denotes the ratio c_{220}/c_{200} , i.e. it is responsible from the deviations from the cylindrical symmetry, q is a measure of the nonextensivity of the system. But it is interesting that they exhibit some similar behaviour about the critical value of the order parameter $\overline{d_{0,0}^{(2)}}$ at the transition.

$\lambda = 0.1$ q	α_K	\overline{P}_2	$\overline{D_{0,2}^2}$	S_c/Nk
0.99	4.458	0.396	0.01719	0.348
0.995	4.481	0.402	0.01716	0.357
1	4.505	0.408	0.0171	0.384
1.005	4.528	0.413	0.017	0.398
1.01	4.551	0.417	0.0169	0.408

Table 1.

$\lambda = 0.2$ q	α_K	\overline{P}_2	$\overline{D_{0,2}^2}$	S_c/Nk
0.99	4.335	0.332	0.0334	0.256
0.995	4.36	0.336	0.0335	0.265
1	4.386	0.341	0.0336	0.275
1.005	4.412	0.348	0.0337	0.301
1.01	4.438	0.354	0.0338	0.314

Table 2.

$\lambda = 0.3$ q	α_K	\overline{P}_2	$\overline{D_{0,2}^2}$	S_c/Nk
0.99	4.104	0.2	0.0399	0.101
0.995	4.132	0.203	0.0404	0.105
1	4.160	0.207	0.041	0.112
1.005	4.1894	0.212	0.0417	0.117
1.01	4.218	0.218	0.0424	0.126

Table 3.

III. CONCLUSION

Many molecular theories assume that an essential characteristic of compounds forming liquid crystals is the rod-like shape of their constituent molecules that means an high length

to breadth ratio. This assumption leads to the approximation that the molecules might be assumed to have cylindrical symmetry. However the molecules, in fact, are lath-like and thus do not possess the high symmetry. In this sense, a molecular theory was developed [10] for an ensemble of such particles based upon a general expansion of the pairwise intermolecular potential together with the molecular field approximation.

Tsallis thermostatics has been commonly employed in studying on the physical systems as a nonextensive statistics and many studies are investigating the nonextensive effects in different systems and phenomena. Thus we would like to handle, in this study, this molecular field theory [10] and to investigate the effects of the nonextensivity for uniaxial nematics formed by non-cylindrically symmetric molecules. With this aim, we investigate the dependence of the long range order parameter on reduced temperature and report the variation of the critical values of the order parameters and entropy change at the transition temperature with the entropic index.

REFERENCES

- [1] A. Saupe, Z. Naturf. A. 19 (1964) 161; P. Diehl and C. L. Khetrapal, NMR Basic Principles Prog. 1 (1969) 1.
- [2] J. A. Pople, Proc. R. Soc. A 221 (1954) 498.
- [3] R. Alben, J. R. McColl, C. S. Shih, Solid St. Commun. 11 (1972) 1081.
- [4] Niederberger, W., Diehl, P., Lunazzi, L., Molec. Phys. 26 (1973) 571.
- [5] M. J. Freiser, Phys. Rev. Lett. 24 (1970) 1041; Liquid Crystals 3, 1972, edited by G. H. Brown and M. M. Labes, Part 1, 281.
- [6] C. S. Shih, R. Alben, J. Chem. Phys. 57 (1972) 3057.
- [7] R. Alben, Phys. Rev. Lett. 30 (1973) 778.
- [8] J. P. Straley, Phys. Rev. A 10 (1974) 1881.
- [9] E. Sackman, P. Krebs, J. U. Rega, J. Voss, H. Möhwald, Molec. Crystals and Liq. Crystals 24 (1973) 283.
- [10] G. R. Luckhurst, C. Zannoni, P. L. Nordio, U. Segre, Mol. Phys. 30 (1975) 1345.
- [11] O. Kayacan, F. Büyükkılıç, D. Demirhan, Physica A 301 (2001) 255.
- [12] O. Kayacan, Physica A 328 (2003) 205.
- [13] O. Kayacan, Chem. Phys. in press.
- [14] M. E. Rose, Elementary Theory of Angular Momentum, John Wiley & Sons, 1957.
- [15] T. D. Shultz, Liquid Crystals, 3, 1972, edited by G. H. Brown and M. M. Labes, Part 1, 263.
- [16] A. Saupe, Angew. Chem. Int. Edition 7 (1968) 97.
- [17] see <http://tsallis.cat.cbpf.br> for an updated bibliography.
- [18] C. Tsallis, J. Stat. Phys. 52 (1988) 479.
- [19] C. Tsallis, R.S. Mendes and A.R. Plastino, Physica A (1998) 534.
- [20] M. S. Reis, J. P. Araújo, V. S. Amaral, E. K. Lenzi, and I. S. Oliveira, Phys. Rev. B 66 (2002) 134417.

- [21] M.S. Reis, J.C.C. Freitas, M.T.D. Orlando, E.K. Lenzi, I.S. Oliveira, Europhys. Lett. 58 (2002) 42.
- [22] E. Dagotto, T. Hotta, A. Moreo, Phys. Rep. 344 (2001) 1.
- [23] M. Mayr, A. Moreo, J.A. Verges, J. Arispe, A. Feiguin, E. Dagotto, Phys. Rev. Lett. 86 (2001) 135.
- [24] A.L. Malvezzi, S. Yunoki, E. Dagotto, Phys. Rev. B 59 (1999) 7033.
- [25] A. Moreo, S. Yunoki, E. Dagotto, Science 283 (1999) 2034.
- [26] J. Lorenzana, C. Castellani, C.D. Castro, Phys. Rev. B 64 (2001) 235127.
- [27] B.M. Boghosian, P.J. Love, P.V. Coveney, I.V. Karlin, S. Succi, J. Yepez, "Galilean-invariant lattice-Boltzmann models with H-theorem", preprint (2002), [e-print: cond-mat/0211093].
- [28] F. Baldovin, A. Robledo, Phys. Rev. E 66 (2002) 045104 (R).
- [29] F. Baldovin, A. Robledo, "Nonextensive Pesin identity: exact renormalization group analytical results for the dynamics at the edge of chaos of the logistic map", preprint (2003), [e-print: cond-mat/0304410].
- [30] A. Beguin, J. C. Dubois, P. Le Barny, J. Billard, F. Bonamy, J. M. Busisine, P. Cuvelier, Sources of thermodynamic data on mesogens, Mol. Cryst. Liq. Cryst. 115 (1984) 1.

IV. FIGURE AND TABLE CAPTIONS

Table 1. The order parameters and entropy change at the nematic-isotropic transition with $\lambda = 0.1$ for some q values.

Table 2. The order parameters and entropy change at the nematic-isotropic transition with $\lambda = 0.2$ for some q values.

Table 3. The order parameters and entropy change at the nematic-isotropic transition with $\lambda = 0.3$ for some q values.

Figure 1. The variation of the order parameters $\overline{d_{0,0}^{(2)}}$ and $\overline{d_{0,2}^{(2)} \cos(2\gamma)}$ with the reduced temperature for some q values, with $\lambda = 0.2$. $q = 1$ represents the Luckhurst et al.'s theory.

Figure 2. The dependence of $\overline{d_{0,2}^{(2)} \cos(2\gamma)}$ on $\overline{d_{0,0}^{(2)}} (= \overline{P_2})$ for various q values.